Dehydration of D-xylose to furfural using selective and hydrothermally stable arenesulfonic SBA-15 catalysts

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ABSTRACT

Furfural (FUR), produced from pentosan-rich biomass, is extensively used as precursor for the furan based chemistry. However, the manufacturing process presents several disadvantages, such as toxic effluents or corrosion issues. Novel heterogeneous catalysts feature high Brönsted acidity and adequate textural-properties to increase FUR selectivity. Modified mesoporous supports have been reported as very appropriate to selectively produce FUR from xylose. This work summarizes the xylose dehydration activity of arenesulfonic SBA-15 catalysts synthesized at high aging-temperature. The SBA-15 catalysts synthesized via co-condensation showed a hexagonal pore arrangement, high arenesulfonic-site incorporation and suitable textural-properties. The activity results in water/toluene revealed that catalysts aged at 180 °C could achieve FUR yield of 80% at 99% conversion on reactions at 160 °C. This was mainly attributed to the high hydrothermal stability of the arenesulfonic-sites and to the porous structure. The catalysts aged at 180 °C showed negligible acid-site leaching effects. The used catalysts were regenerated by a thermal treatment at 290 °C and these showed good reusability on repetitive runs at the investigated reaction-temperatures. However, the catalysts aged at lower temperatures showed important deactivation rates.

1. Introduction

In the past years, several environmental and economic issues related to petroleum-derived fuels and chemicals have arisen, so the interest for the design of biorefineries has renewed [1]. The concept of biorefinery makes use of raw biomass as the starting precursor for the production of biofuels and bio-based products. In this sense, second generation fuels can directly affect the feasibility of integrated strategies to use lignocellulosic wastes as biochemical source [2].

Furfural (FUR) is widely used as an industrial solvent and shows potential applications as building-block to produce higher added-value products, such as methyltetrahydrofuran or levulinic acid [3]. It is currently manufactured from pentosan-rich biomass under homogeneously acid-catalyzed conditions (Scheme 1). In order to increase its production yield, FUR self-resinification and secondary reactions with intermediates (I) are minimized by steam-stripping. However, these processes suffer from severe corrosion and toxic effluent issues, together with high product/catalyst separation costs. The current FUR production processes reach an overall yield of 50% [4]. Alternative process-optimization studies focused on

rapid FUR quenching by flash decompression at high temperature [5], nitrogen-stripping [6] or extraction with using different water/organic biphasic systems [7]. FUR production process clearly shows that green chemicals should be based not only on renewable biomass feedstock, but also on green production processes.

Recent research studies to produce FUR from D-xylose focused on the synthesis of hydrothermally stable heterogeneous acids due to the ease of their post-reaction separation and reutilization. These catalysts were featured by high Brönsted acidity and adequate shape selectivity at high conversion values for enhanced productivity. Valente and co-workers prepared several solid acid catalysts, ranging from conventional sulfated zirconia [8], exfoliated nanosheets [9] or silicoaluminophosphates [10]. Other studies were focused on using zeolitic structures such as ZSM-5 [11], mordenite/faujasite-HY type arrangements [12], layered zeolites with high active site accessibility [13] or metal oxides using biomass [14]. Among the mesoporous catalysts, modified MCM-41 supports [15,16] or sulfonated silica shells [17] showed high activity. Based on the studies using functionalized SBA-15 catalysts for xylose dehydration [18], sulfonic SBA-15 catalysts with controlled pore size tuning were also reported [19]. The controlled synthesis conditions allowed to maximize the FUR yield (FUR$_Y$) up to 82% at 170 °C of reaction temperature.

One of the most important issues related to heterogeneous acid catalysts deals with the stability of the active sites and

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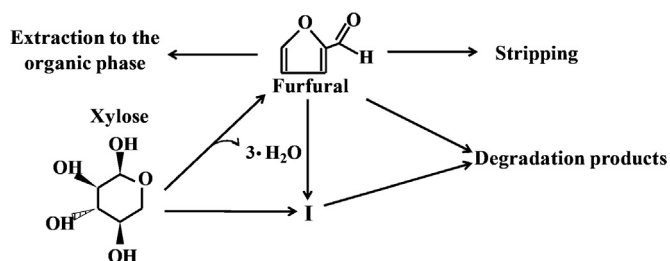
Scheme 1. Acid-catalyzed reactions during the production of furfural from xylose.

their recyclability. As proved with functionalized SBA-15 catalysts, post-reaction acidity can be considerably decreased under hydrothermal conditions [19]. These data proved that the sulfonic sites are destabilized in water/toluene systems under more severe reaction temperatures than their synthesis conditions. Arenesulfonic-derived sites showed higher stability than propylsulfonic sites, but overall acidity decreased considerably during reaction. Similar acid-site leaching phenomena in water/toluene were observed for some of the catalysts reported in the literature [20], whereas materials such as inorganic oxides [8,21], vanadium phosphates [22], Beta/TUD-1 composites [23] or Nafion catalysts [24] showed higher stability and recyclability.

For these reasons, the design of hydrothermally stable and active SBA-15 sulfonic catalysts is an interesting alternative to carry out the dehydration of xylose, combining optimized textural-properties with stable acid-sites. As previously reported, SBA-15 supports have been synthesized combining the copolymer Pluronic 123 and the fluorocarbonated FC-4 surfactant to create highly stable SBA-15 materials (JLU-20) [25]. Recent studies focused on the use of mesoporous JLU supports for hydroxylation using Ti-JLU materials [26] or Fe-JLU for Friedel–Crafts alkylations [27]. On the other hand, propylsulfonic sites were also grafted by co-condensation for JLU-20 catalysts. Feng et al. [28] synthesized materials with high structural crystallinity and sulfonic loading, obtaining activities comparable to liquid concentrated H_2SO_4 in organic solvents (such as cyclohexanol esterification), where leaching effects are minimized. To our knowledge, there are no published data on the characterization and hydrothermal stability of arenesulfonic SBA-15 catalyst aged at high-temperature and their application to the production of FUR from xylose.

Thus, this work aims to give a new input to the synthesis of functionalized mesoporous SBA-15 catalysts and their application to the D-xylose dehydration with a special emphasis on their hydrothermal stability. Even if toluene is not a green chemical, it shows very suitable properties to extract FUR from the water medium. Future potential applications of the studied catalysts should be applied using water as solvent and FUR separation throughout green stripping [6]. The studied materials will be modified using arenesulfonic and propylsulfonic precursors at different aging-temperatures to achieve tailored textural-properties [29] and thus evaluate its effect on the catalytic activity, sulfonic incorporation and acid-site stability at different reaction temperatures. Finally, post-reaction structural stability and catalyst recyclability will be also studied.

2. Materials and methods

2.1. Catalyst preparation

2.1.1. Arenesulfonic SBA-15 via co-condensation

The arenesulfonic groups were incorporated into SBA-15 supports following the recipe described in the literature [30]: 4 g of Pluronic 123 (PEO-PPO-PEO copolymer – *Aldrich*) were first dissolved in 125 mL of HCl (1.9 M) at room temperature. The solution was heated to 40 °C before the dropwise addition of tetraethylorthosilicate (TEOS – *Aldrich*). A prehydrolysis time of 180 min was here established. The sulfonic precursor CSPTMS (2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane – *Acros Organics*) was added at once together with the oxidizing agent (H_2O_2 30 wt.% – *Aldrich*). The molar composition of the mixture for 4 g of P123 was 0.0369 TEOS:0.0092 CSPTMS:0.0123 H_2O_2:0.24 HCl:6.67 H_2O. This way, a CSPTMS/(TEOS + CSPTMS) organosiloxane molar load of 0.20 was set. The resulting solution was hydrolyzed at 40 °C for 20 h under stirring and later transferred into a Teflon lined autoclave for aging. The aging conditions were set at 100 °C for 24 h under static conditions. The solid product was recovered by filtration, washed thoroughly with water and dried at room temperature. The P123 template present in the silica structure was extracted with ethanol under reflux (1.5 g of as-synthesized material per 400 mL of ethanol). The solid product was filtered, washed with ethanol and dried. This material was named as A100-0.20.

2.1.2. Highly stable arenesulfonic SBA-15 via co-condensation

Novel highly stable arenesulfonic SBA-15 catalysts were prepared modifying the recipe described in the literature [30] using fluorocarbonated (FC-4) surfactants [25]: 1.66 g of Pluronic 123 and 5 g of FC-4 (*Acros Organics*) were first dissolved in 200 mL of HCl (1.9 M) at room temperature. TEOS was first prehydrolyzed (180 min) and then the CSPTMS and H_2O_2 (30 wt.%) were added. The resulting solution was hydrolyzed at 40 °C during 20 h. The molar composition of the mixture for 1.66 g of P123 and 5 g of FC-4 was 0.0616 TEOS:0.0154 CSPTMS:0.0205 H_2O_2:0.3811 HCl:10.35 H_2O. This way, a CSPTMS/(TEOS + CSPTMS) organosiloxane molar load of 0.20 was set. The resulting solution was hydrolyzed at 40 °C for 20 h under stirring and later transferred into a Teflon lined high-pressure reactor (*Berghof*). The aging-temperature was slowly increased for 10 h up to 160–180 °C and maintained there for 30 h under static conditions and autogenous pressure. The solid product was filtered and extracted as previously described. The materials were labeled as AX-0.20 where X is the corresponding aging-temperature (°C). Catalysts with higher arenesulfonic precursor loading were prepared as AX-0.20 samples by increasing the CSPTMS/(TEOS + CSPTMS) ratio from 0.20 to 0.33 and 0.43.

2.1.3. Highly stable propylsulfonic SBA-15 via co-condensation

Based on the same recipe described in Section 2.1.2, the sulfonic precursor was changed to mercaptopropyltrimethoxysilane (MPTMS), by keeping a MPTMS/(TEOS + MPTMS) ratio of 0.20. The sample was denoted as PX-0.20.

2.2. Catalyst characterization

N_2-physisorption isotherms of as-extracted SBA-15 catalysts were obtained at 77 K over the whole range of relative pressures, using an Autosorb 1C-TCD (*Quantachrome*) automatic device and samples previously outgassed at 423 K for 12 h. The specific surface-area was calculated using the Brunauer–Emmett–Teller (S_{BET}) method while the micropore volume was estimated by the t-plot method. The pore size distribution (PSD), the total pore volume (V_P) and mean pore diameter (D_P) were derived using the Barrett–Joyner–Halenda (BJH) method.

Transmission electron microscopy (TEM) micrographs were taken on a Phillips CM200 microscope equipped with a LaB6 filament and a supertwin lens operating at 200 kV. Bright field images were acquired using a CCD camera (*TVIPS GmbH*). Scanning electron microscopy (SEM) studies were carried out on a JEOL JSM-7000F with field emission cathode operating at 20 kV. NMR spectra were obtained using a Bruker 400 WB Plus spectrometer. Spectra were collected using a 4 mm CP-MAS probe at a spinning of 10,000 Hz.

^{29}Si NMR spectra of solid samples were recorded for 12 h using the standard pulse sequence, at 79.5 MHz, a time domain of 1 K, a spectral width of 55 kHz, a contact time of 2 ms and an interpulse delay of 5 s.

Ion-exchange capacities (mmol H$^+$/g SiO$_2$) were determined using 0.05 M of tetramethylammonium chloride (TMACl) as exchange agent. In a typical measurement, 0.05 g of SBA-15 catalyst was suspended in 10 g of the mentioned solution and equilibrated for 18 h. The resulting solution was titrated potentiometrically by dropwise addition of 0.01 M NaOH. Thermogravimetric analyses (TGA) were carried out in a TGA/SDTA 851e module (*Mettler-Toledo*), measuring the weight variation during oxidation at a heating ramp of 10 °C min^{-1} from room temperature until 800 °C.

2.3. Catalytic tests

Xylose dehydration batch catalytic tests were performed in a temperature-controlled stain-steel reactor (*Autoclave Engineers*) stirred at 500 rpm. In order to keep the reaction medium in liquid-phase (200 mL of reaction total solution), the system was pressurized at 15 bar. The water/toluene tests were performed with 1:1 (v/v) water/toluene ratio (mol ratio of 5.9 water/toluene). The corresponding xylose solution was pumped with a Waters 515 pump to obtain an initial xylose load of 20 g L^{-1}. Catalyst load was fixed at 60 wt.% with respect to initial xylose load and reaction time was set at 20 h. In order to study the stability of functionalized SBA-15, the solid catalysts were recovered by filtration, washed thoroughly with water to remove impurities and dried at room temperature.

The products and the unreacted xylose were quantified using a HPLC module ICS-3000 from *DIONEX* coupled to an AS40 Autosampler. FUR was quantified using a Kinetex C18-XB 4.6 mm × 150 mm column from *Phenomenex* at 40 °C coupled to a UV-2070 Plus detector from *JASCO* at 280 nm wavelength. The mobile phase was pumped at 1 mL min^{-1} and consisted of 0.01 M H$_2$SO$_4$ and 10% (v/v) acetonitrile aqueous solution. Xylose was quantified using a CarboPac PA20 3 mm × 150 mm column, at 30 °C and 0.5 mL min^{-1}, using 8 mM of NaOH as mobile phase. Detection was carried out using an electrochemical cell with integrated amperometry and Standard Carbohydrate Quad method.

The definition of xylose conversion (X_X), FUR selectivity (FUR$_S$) and FUR yield (FUR$_Y$) are as follows:

$$X_X \ (\%) = 1 - \frac{\text{mol of xylose at time } t}{\text{initial mol of xylose}}$$

$$\text{FUR}_S \ (\%) = \frac{\text{mol of FUR at time } t}{\text{mol of converted xylose}}$$

$$\text{FUR}_Y \ (\%) = X_X \cdot \text{FUR}_S$$

3. Results and discussion

3.1. Arenesulfonic catalyst characterization

The main physicochemical properties of fresh catalysts were measured by N$_2$-physisorption for textural-properties and by TMACl equilibration for the determination of catalyst acidity, respectively (see Table 1). The influence of the aging-temperature on the textural-properties was previously reported as determinant to create materials with different porosity [19]. When the materials are aged over 130 °C (A160-0.20/A180-0.20) the P123 copolymer starts to decompose [28]. After 130 °C, the hexagonal arrangement provided by P123 is still conserved, but the samples suffer a considerable decrease in S_{BET} and D_P compared to A100-0.20.

Table 1
Physicochemical properties of fresh Amberlyst 70 and functionalized SBA-15 catalysts.

| Catalyst	S_{BET} (m^2/g)	D_P (Å)	V_P (cm^3/g)	Acidity (mmol H$^+$/g)
Amberlyst 70	2	–	–	2.55
A100-0.20[a]	747	82.0	1.04	1.17
A160-0.20[a]	413	40.2	0.64	0.92
A180-0.20[a]	387	37.2	0.53	0.95
P180-0.20[b]	287	29.1	0.46	0.99

Average S.D. characterization: 3.2%.
[a] Organosiloxane molar load = 0.20 (CSPTMS/CSPTMS + TEOS).
[b] Organosiloxane molar load = 0.20 (MPTMS/MPTMS + TEOS).

All N$_2$-physisorption isotherms were of type IV and exhibited H1 hysteresis loops (Fig. 1). These types of isotherms are common for hexagonal mesoporous arrangement such as SBA-15 or MCM-41. In all the cases, the pore-filling step in adsorption and desorption was sharp, showing a narrow PSD. The slope of the pores filling after the low-pressure step was smaller for A160-0.20 and A180-0.20, provoking a deep decrease in the S_{BET}: from 747 m^2/g for A100-0.20 to ~400 m^2/g (A160-0.20 and A180-0.20), as reported in the literature [28]. The V_P, measured as the maximum mesopore filling, was also higher for A100-0.20, as well as the D_P (Table 1). However, the decomposition of the P123 template over 130 °C produced a decrease of the final pore size. D_P values were reduced from 82 Å (A100-0.20) to ~40 Å (A160-0.20 and A180-0.20). According to the PSD data, the micropores tended to vanish for samples aged at 160 and 180 °C.

As indicated by the acidity measurements shown in Table 1, and even if the initial organosiloxane load was the same for all samples, acid-site incorporation slightly decreased at high aging-temperatures. However, these differences were within the expected range. Moreover, these variations were previously reported as negligible to evaluate the xylose dehydration activity [19]. The acidity measurements were also checked by NH$_3$-TPD measurements, showing surface acidity around 1 mmol H$^+$/g (Fig. A2). The FTIR spectra of pyridine adsorbed on the arenesulfonic catalysts showed a broad peak centered at 1545 cm^{-1}, corresponding to Brönsted acids (Fig. A3). No Lewis centers were detected for these samples. Indeed, the ratio of Brönsted to Lewis centers was reported as determinant to achieve high FUR$_Y$ values [21]. The dTGA profiles (indicative of total weight loss) of fresh arenesulfonic materials are shown in Fig. 2a. Even if relative weight derivative differences were evident, the fraction of overall acid-site weight-loss was similar for all samples. A160-0.20 and A180-0.20 showed more defined desorption peaks centered ~500 °C. Along the TGA
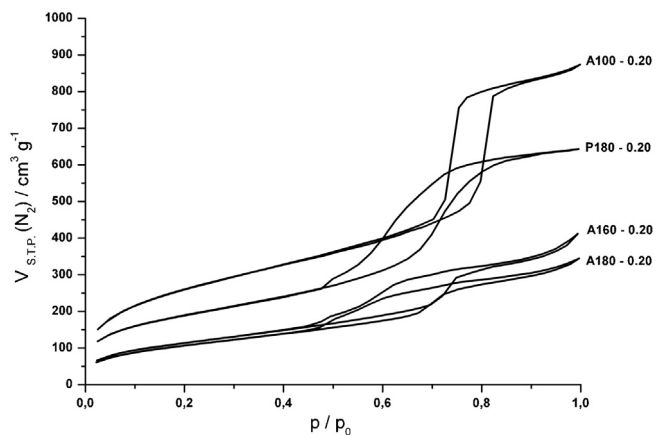
Fig. 1. N$_2$-physisorption isotherms of arenesulfonic and propylsulfonic SBA-15 catalysts synthesized via co-condensation at different aging-temperatures.
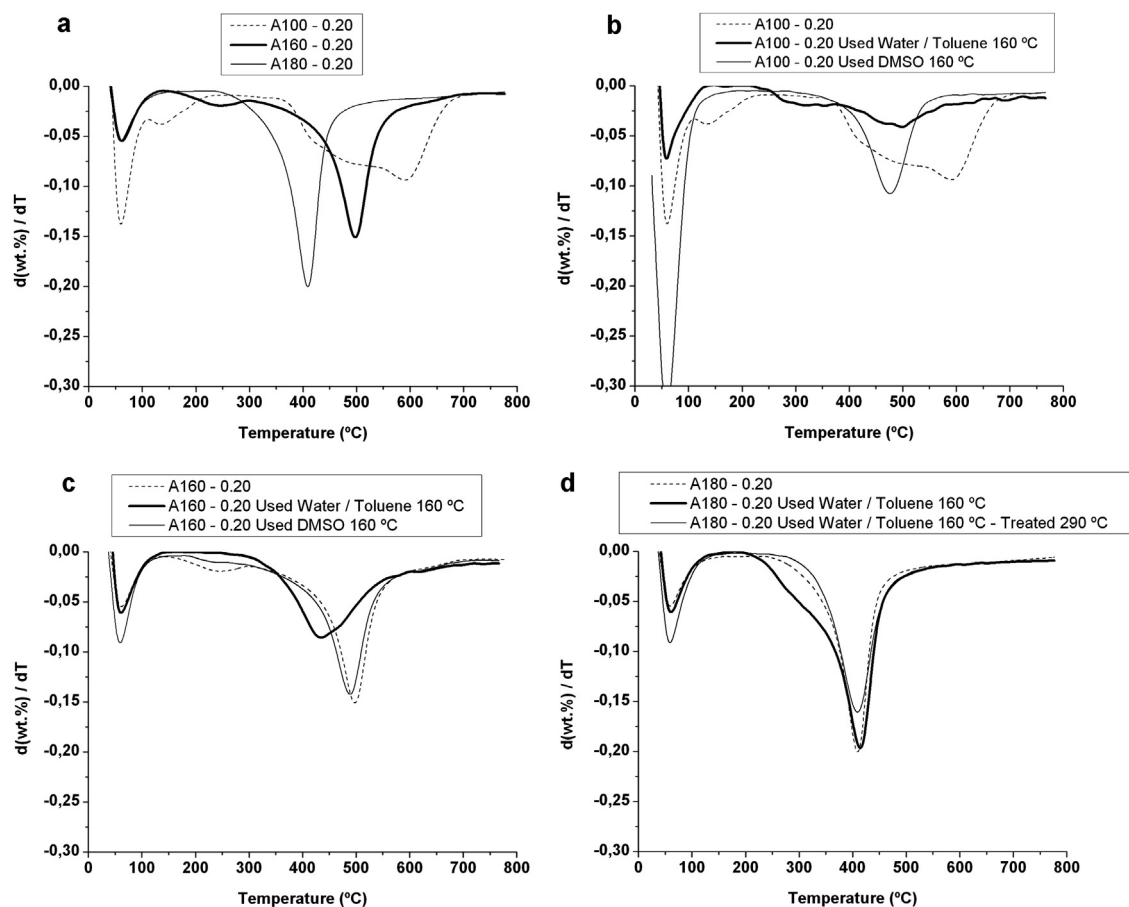
Fig. 2. TGA profiles of fresh and used arenesulfonic SBA-15 catalysts synthesized at different aging-temperatures.

process, physisorbed water was first desorbed from 60 to 130 °C. When the samples were further heated, the sulfonic sites were probably decomposed as SO or SO_2. However, no TGA-MS analyses were carried out to detect the product distribution during sample decomposition.

The SEM and TEM images of fresh A180-0.20 are depicted in Fig. 3. The front view of the catalyst showed the honeycomb-like hexagonal arrangement of the cylindrical pores. Comparing these data to lower temperature-aged materials [19], it seemed that high aging-temperatures barely affected to the structural crystallinity of the arenesulfonic SBA-15 catalysts. The top view clearly showed the arrangement of the cylindrical pores. Similar mesopore arrangements were achieved for A100-0.20 and A160-0.20 catalysts. According to the solid-state ^{29}Si NMR spectra, the structural properties of conventional SBA-15 matrix were also preserved for the arenesulfonic SBA-15 catalysts (Fig. 4). During aging, the silanol groups were dehydrated to give siloxane groups. In the arenesulfonic SBA-15 catalysts, distinct resonances could be monitored for siloxane (Q^n, where $n = 2$–4 for Q^4 at -110.6 ppm, Q^3 at -101.1 ppm and Q^2 at -90.9 ppm). Organosiloxane moieties (T^2 and T^3 groups) on the silica surface were also observed at ~-66 ppm. Proton (H) NMR spectra (not shown here) showed as well the presence of a strong peak centered at 3.95 ppm, confirming the presence of aryl rings on the silica surface.

3.2. Activity and stability of arenesulfonic catalysts

The activity of the arenesulfonic catalysts was evaluated at different reaction temperatures in water/toluene (based on the Maers' criterion calculations [31], the limitation associated to external

diffusion could be neglected). As depicted in Fig. 5, initial xylose conversion and FUR_S values at 160 °C were similar for all catalysts. However, after 6–8 h of reaction, A100-0.20 and A160-0.20 suffered a decrease on the xylose dehydration activity. Xylose was converted at higher rate for A180-0.20 after this point. The coke deposits on the acid-surface reduced considerably the catalytic activity for non-stable catalysts (A160-0.20 and especially the A100-0.20 sample). The A100-0.20 sample at 6 h showed a TOF value of 1.02 mmol $[H^+]^{-1}$ h^{-1} at 160 °C, whereas A160-0.20 and A180-0.20 were also in the same order of magnitude (1.01 and 1.05). On the other hand, FUR_S values (Fig. 5b) were higher for A180-0.20, showing the importance of the sulfonic-site stability to maximize the FUR production on long-time reactions. Fig. 6 summarizes the FUR_Y of different catalysts at 20 h for different reaction-temperatures. It was previously reported that Brönsted catalysts with poor S_{BET} (Amberlyst 70) led to fast secondary-reaction rates [6]. As observed in Fig. 6, FUR_Y could be maximized at 160 °C for all catalysts, while faster reaction rates (at 180 °C) led to more enhanced yield-loss reactions (see evolution on time for A180-0.20 at different temperatures in Fig. A1). The highest FUR_Y value (82%) was achieved for A180-0.20 at 160 °C of reaction temperature. In general, clear FUR_Y differences were observed among arenesulfonic SBA-15 catalysts, mainly due to the stability of the acid-sites all along the reactions. Reactions at 140 °C were probably not favorable due to low reaction rates together with low diffusivity of reactants to the active sites. The overall diffusivity values (calculated from the molecular and Knudsen coefficients [32]) were in the order of 0.055 cm^2/s for the A100-0.20 sample and 0.033 cm^2/s for the A160-0.20 and A180-0.20 at 160 °C. This suggested that the bigger D_P on A100-0.20 enhanced the diffusion of xylose and furfural into them,
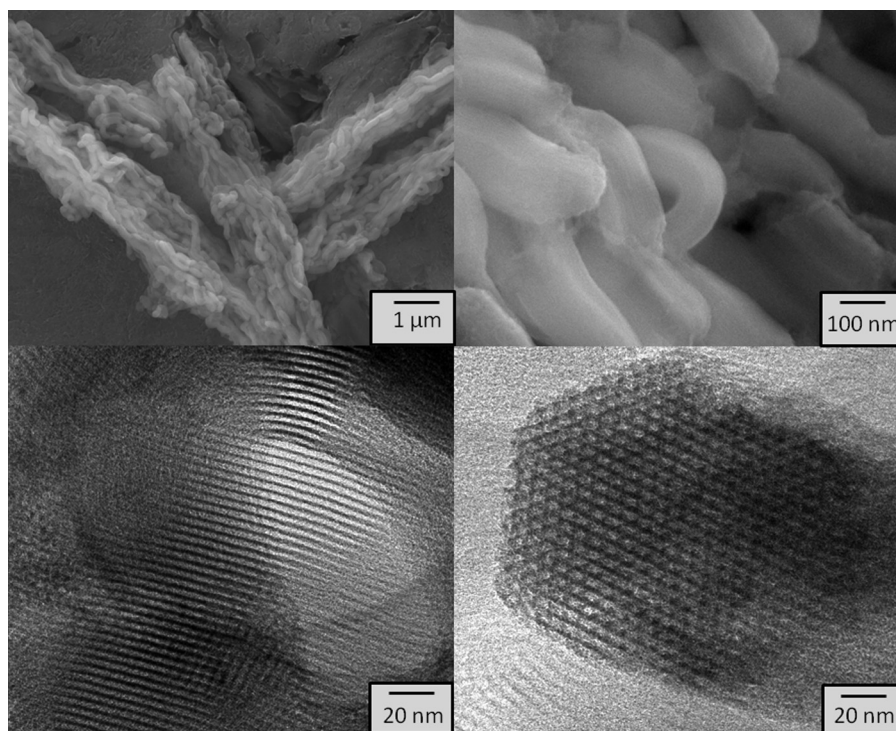
Fig. 3. SEM and TEM images of fresh A180-0.20.

leading to more yield-loss reactions. On the other hand, resinification/condensation reactions were enhanced at 180 °C (maximum FUR_Y of 65% for A180-0.20).

As checked in Fig. 2a, the arenesulfonic groups showed the biggest decomposition peak starting at 300 °C for A180-0.20. For this reason, and in order to neglect the effect of the residual coke on the acidity measurements, the used catalysts were treated at 290 °C in air. This way, most of the coke deposits on the sulfonic sites were decomposed, and the physicochemical properties of the used materials could be correctly compared to the fresh ones. Further tests with non-treated used samples proved that catalysts without accessible surface sites, due to deposited-coke, showed lower FUR_Y (~55%) than stable acid-sites at the same xylose conversion values. As proved in the literature [15], the coke-deposited catalysts acted as inert supports, where xylose was protonated and dehydrated due to the presence of the H_3O^+ coming from the reaction medium (water). This enforced the idea that used catalysts should be thermally treated to preserve the initial physicochemical properties of the fresh ones. This was not the case for other sulfonic modified catalysts reported in the literature [15,18], where the acid-group thermal stability was limited to lower thermal treatment temperatures (~250 °C).

The acidity of the used catalysts, as observed in Fig. 7a, was just preserved for the samples aged at high temperature. A100-0.20 showed a deep decrease in its acidity (Fig. 2b). This was the main reason to achieve lower FUR_Y than A160-0.20 and A180-0.20. According to Fig. 7a, A160-0.20 acid-sites were not deactivated at 160 °C in water/toluene, while its surface acidity dropped from 0.89 to 0.79 mmol H^+/g after reactions at 180 °C. It seems that the hydrolytic attack at 180 °C enhanced the cleavage of the aryl ring—silica bond. On the other hand, the deactivation of A180-0.20 acid-sites during the studied temperatures was much lower than for the rest of catalysts. The increase of the aging temperature, facilitated by the presence of FC-4, increased the sulfonic-site stability. The treated used catalysts showed a C content increase from 3.1 (fresh) to 3.5%, corresponding to residual coke. However, the acidity measurements proved that the thermal treatment could effectively remove the carbon deposits on the acid-sites. Even if there were no significant structural differences between A160-0.20 and A180-0.20, their acid-site stability difference was determinant to obtain different FUR_Y values. On the other hand, Brönsted Amberlyst 70 catalyst led to strong FUR_Y drops by the end of the tests. Comparing SBA-15 (S_{BET} ~ 400 m^2/g) and Amberlyst 70 (S_{BET} ~ 1 m^2/g), it could be concluded that not only the nature (Lewis/Brönsted) [21] or the stability of the acid-sites (40% sulfonic-site loss for Amb70) are important during xylose dehydration, but also the textural-properties of the catalyst surface.
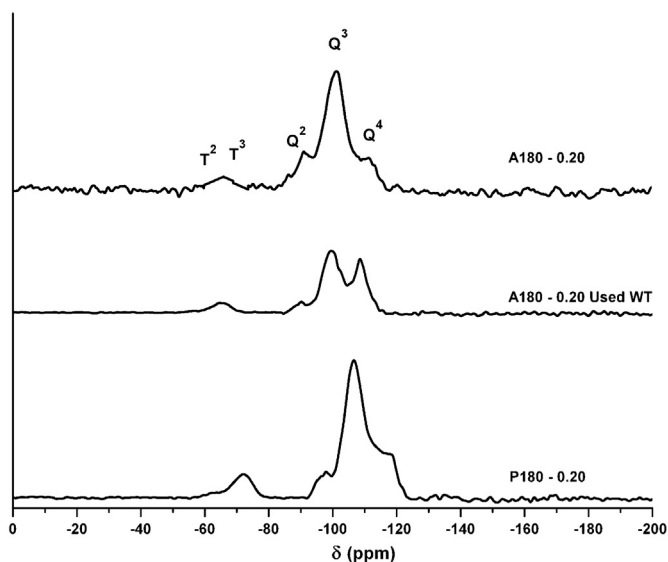

Fig. 4. ^{29}Si NMR spectra of fresh A180-0.20, used A180-0.20 (in water/toluene at 160 °C and treated at 290 °C) and fresh P180-0.20. Q^n and T^m moieties calculated from the relative integrated intensities (T^m/Q^n).
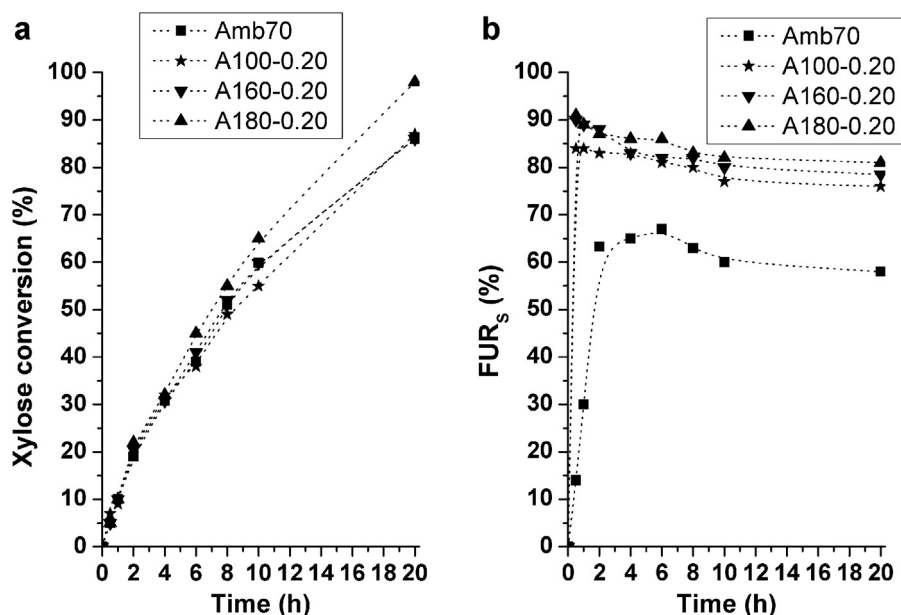
Fig. 5. Evolution on time of the xylose conversion and the FUR_Y for Amberlyst 70 and functionalized SBA-15 catalysts at 160 °C in water/toluene. S.D.: 4.6%.

The structural stability was also evaluated by N_2-physisorption, as shown in Fig. 7b. Despite the aggressive hydrothermal reaction conditions, the structural stability provided by the siloxane bonds was high. A160-0.20 and A180-0.20 showed slight differences in the S_{BET} values (2% reduction). This could be attributed to blocked pores due to coke deposits or to the high structural tension created during the mesopore drying. The highest structural shrinkage occurred for A100-0.20 (568 m^2/g in water/toluene). The A100-0.20 PSD data showed a reduction of the D_P from 55 to 35 Å, as well as a reduction of 52% in the V_P. The hexagonal cylindrical shape was also preserved for all arenesulfonic SBA-15 catalysts after the strong hydrothermal reaction conditions, as checked by TEM analysis (not shown). According to the ^{29}Si NMR spectra, structural integrity (Q and T groups) was also preserved for A180-0.20 after reactions at 160 °C in water/toluene and further treatments at 290 °C (Fig. 4).
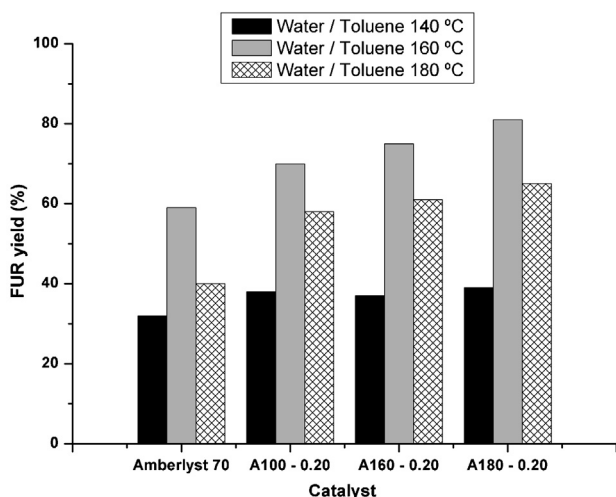

Fig. 6. FUR_Y using Amberlyst 70 and arenesulfonic SBA-15 catalysts during xylose dehydration in water/toluene.

3.3. Effect of the arenesulfonic loading

Catalysts with higher arenesulfonic loadings were prepared in order to evaluate the sulfonic load effect on the activity. The organosiloxane load was increased from 0.20 to 0.33 (A180-0.33) and to 0.43 (A180-0.43). The sample A180-0.33 was correctly synthesized, even if the initial mixture gel was very viscous. However, the synthesis of A180-0.43 could not be completed. After the hydrolysis step, the mixture became very thick, complicating the aging process. For this reason, just the activity of A180-0.33 was here evaluated. It has to be noted that Feng et al. reported highly stable propylsulfonic JLU-20 materials with an organosiloxane load as high as 0.80 [28].

According to the acidity measurements, A180-0.33 showed the same acid-site content as A180-0.20 (Table 2). The D_P values showed a strong drop: from 55 Å (A180-0.20) to 23 Å (A180-0.33). The interference of more aryl molecules during the mesophase formation clearly reduced the final D_P. However, this sulfonic loading increase affected only the xylose dehydration activity at 140 °C (Table 2). The X_X and TOF values of A180-0.33 were higher than the ones showed by A180-0.20 (TOF values increased from 0.69 to 0.81 mmol [H$^+$]$^{-1}$ h^{-1}), suggesting that a lower acid-site density (based on acidity and S_{BET} values, this is 1.5 lower for A180-0.33) could increase the xylose conversion rate. On the other hand, the highest FUR yield was obtained at 160 °C of reaction temperature, similar to A180-0.20 (final X_X = 99% and FUR_Y = 86% at 160 °C).

3.4. Activity and stability of propylsulfonic catalysts

As proved in the literature [28], the propylsulfonic JLU-20 catalysts could be synthesized using the same recipe as the arenesulfonic ones. The sample P180-0.20 showed a typical isotherm IV with a H1 hysteresis loop and lower S_{BET} (287 m^2/g) and D_P (29 Å) than A180-0.20 (Fig. 1). On the other hand, the surface acidity was similar (0.99 mmol H$^+$/g). NMR spectra showed the presence of siloxane (Q^n) as well as organosiloxane (T^m) groups on the P180-0.20 surface (Fig. 4).

In a previous work [19], a preliminary catalyst screening showed that propylsulfonic sites were more selective than arenesulfonic.
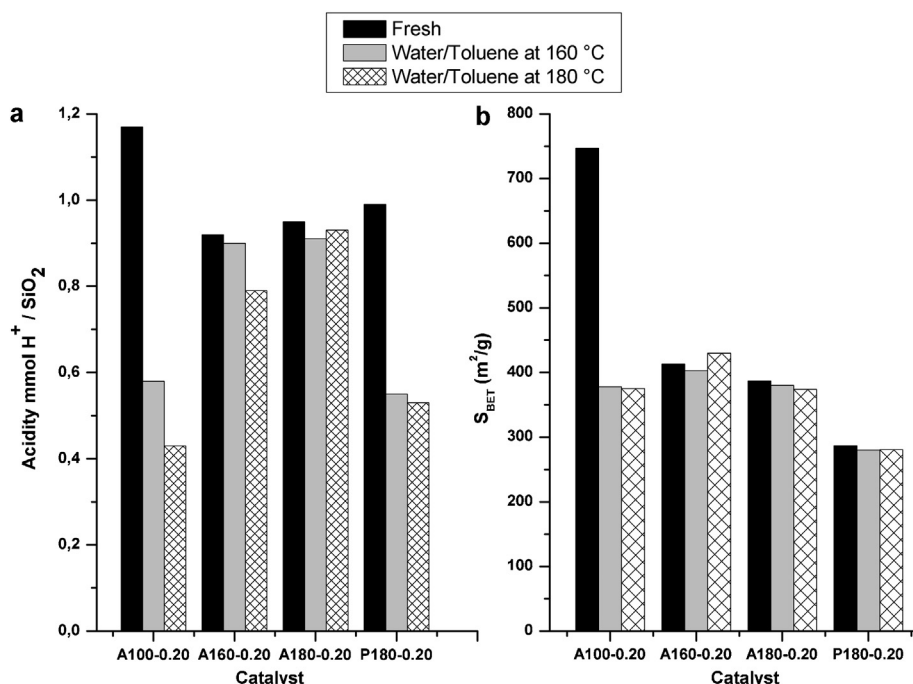
Fig. 7. Stability of the acid-sites and the S_{BET} of arenesulfonic and propylsulfonic SBA-15 catalysts tested during xylose dehydration in water/toluene.

This work showed the same case for reactions carried out at 140 °C, where P180-0.20 could achieve a FUR$_Y$ maximum of 80% at 85% of X_X (Table 2). However, higher reaction temperatures proved that these catalysts were less selective (FUR$_Y$ 60%) at 180 °C. This was mainly attributed to a lower stability of the propylsulfonic sites as compared to arenesulfonic (Fig. 7a). Even at reaction-temperatures lower than the aging, the acidity of P180-0.20 dropped from 0.99 (fresh) to 0.55 mmol H$^+$/g (used). This difference proved that the high electron density of the aryl ring gave an additional stability compared to the propyl chain. To prepare SBA-15 derived stable catalysts under hydrothermal conditions, the reported and discussed data clearly support that not only the aging-temperature is important, but also the nature of the sulfonic precursor.

3.5. Catalysts reusability

The reusability is one of the most relevant parameters to evaluate the feasibility of a heterogeneous catalyst for different catalytic applications. In this case, used catalysts and treated in air at 290 °C were recycled without any further step (denoted as AX-0.20R$_N$). The reusability was studied at 160 and 180 °C, proved as the temperatures where the highest FUR$_Y$ and acid-site leaching effects were obtained (Table 3). Fresh A180-0.20 showed the highest FUR$_Y$ at 160 °C, and A180-0.20R$_1$ showed the same trend. A100-0.20R$_1$ FUR$_Y$ dropped to 67%, while A160-0.20R$_1$ was maintained at 78%. The TOF values for A160-0.20R$_1$ were slightly reduced, while A100-0.20R$_1$ deactivation showed a strong TOF drop. The A180-0.20R$_1$ sample was further recycled at 160 °C (A180-0.20R$_2$), and the results showed that it could again achieve high X_X (88%) and FUR$_Y$ (75%). The acidity of A180-0.20R$_2$ was 0.88 mmol H$^+$/g. The fourth repetitive run at 160 °C showed a decrease on xylose conversion and FUR yield, even if it preserved high surface acidity (0.83 mmol H$^+$/g). Each repetitive run showed a catalyst loss of 0.1 g at the recovery (on reactor walls and stirrer). The conversion and yield drop could be attributed to the experimental error given by the use of lower catalyst (and thus less xylose mass) than in previous tests. On the other hand, the reactions at 180 °C showed a complete xylose conversion for all samples, but the low FUR$_S$ of A100-0.20R$_1$ and A160-0.20R$_1$ also resulted in lower final FUR$_Y$. In this case, the

Table 2
Catalytic activity of fresh arenesulfonic and propylsulfonic SBA-15 catalysts during xylose dehydration to furfural in water/toluene.

Catalyst	S_{BET} (m²/g)	Water/toluene at 140 °C				Water/toluene at 160 °C			Water/toluene at 180 °C		
		Acidity (mmol H$^+$/g)	X_X [d] (%)	FUR$_Y$ [e] (%)	TOF [f] (mmol (mequiv. H$^+$)$^{-1}$ h^{-1})	X_X [d] (%)	FUR$_Y$ [e] (%)	TOF [f] (mmol (mequiv. H$^+$)$^{-1}$ h^{-1})	X_X [d] (%)	FUR$_Y$ [e] (%)	TOF [f] (mmol (mequiv. H$^+$)$^{-1}$ h^{-1})
A180-0.20[a]	387	0.95	65	60	0.69	98	82	1.05	97	65	1.15
A180-0.33[b]	568	0.94	76	71	0.81	99	86	1.11	99	66	1.11
P180-0.20[c]	287	0.99	85	80	1.04	94	79	1.01	98	60	1.09

Average S.D. catalytic tests: 4.1%.
[a] Organosiloxane molar load = 0.20 (CSPTMS/CSPTMS + TEOS).
[b] Organosiloxane molar load = 0.33 (CSPTMS/CSPTMS + TEOS).
[c] Organosiloxane molar load = 0.20 (MPTMS/MPTMS + TEOS).
[d] Conversion of xylose after 20 h.
[e] FUR yield after 20 h.
[f] Turnover frequency (TOF) calculated from mmol of converted xylose at 6 h of reaction (~40% of final X_X).

Table 3
Catalytic activity of fresh and recycled arenesulfonic and propylsulfonic SBA-15 catalysts during xylose dehydration to furfural in water/toluene.

Catalyst	Water/toluene at 160 °C		Water/toluene at 180 °C	
	FUR_Y [b] (%)	TOF [c] (mmol (H$^+$)$^{-1}$ h^{-1})	FUR_Y [b] (%)	TOF [c] (mmol (H$^+$)$^{-1}$ h^{-1})
A100-0.20	69	1.02	58	1.07
A100-0.20R$_1$ [a]	67	0.81	59	1.05
A160-0.20	76	1.01	61	1.06
A160-0.20R$_1$ [a]	78	0.93	62	1.02
A180-0.20	82	1.05	65	1.15
A180-0.20R$_1$ [a]	82	0.99	73	1.06
A180-0.20R$_2$ [a]	75	0.88	–	–
A180-0.20R$_3$ [a]	70	0.79	–	–
P180-0.20	79	1.01	60	1.09
P180-0.20R$_1$ [a]	58	0.84	47	1.06

Average S.D. catalytic tests: 4.5%.

[a] Catalysts recycled after thermal treatment at 290 °C. The R_N states for the number of the recycling run.
[b] FUR yield after 20 h.
[c] Turnover frequency (TOF) calculated from mmol of converted xylose at 6 h of reaction (~40% of final X_X).

TOF values were nearly independent of the type of catalyst. The propylsulfonic P180-0.20 was also reused at 160 and 180 °C, but its poor sulfonic stability provoked a strong decrease on the final FUR_Y (~55%).

According to the stability data reported in the literature, the propylsulfonic materials prepared by Shi et al. [18] showed the same S content after their use and H_2O_2 regeneration, at 4 h of reaction time. We reported 40% of sulfonic-site loss at 6 h of reaction time [19] using the same aging temperature (100 °C). Reaction periods of up to 20 h led to almost complete sulfonic-site deactivation. On the other hand, this work proved that SBA-15 supports functionalized with arenesulfonic precursors and aged at higher temperatures show a long-term hydrothermal acid-site stability and recyclability.

4. Concluding remarks

The incorporation of the arenesulfonic precursor was correctly carried out on SBA-15 supports at high aging-temperatures. The procedure developed for the synthesis of highly stable arenesulfonic SBA-15 catalysts has been evaluated during the xylose dehydration at different reaction temperatures. The activity tests showed an optimum reaction temperature of 160 °C for the most suitable arenesulfonic SBA-15 catalyst (A180-0.20). The furfural yield could be maximized to 82%. The nature of the sulfonic precursor and aging-temperature were proved to be determinant, since just the acidity of A180-0.20 was preserved nearly intact for the investigated reaction-temperatures, while significant leaching effects were observed for catalysts aged at lower temperature or other sulfonic precursors. The SBA-15 catalysts were regenerated by using a thermal treatment at 290 °C. The post-reaction S_{BET} and acid-site contents were maintained even after three consecutive runs, obtaining a furfural yield of 75% at 88% of xylose conversion.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcatb.2012.11.010.

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